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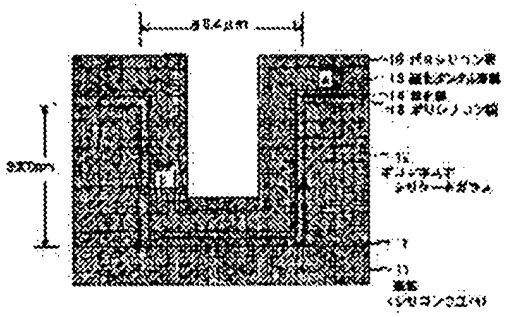
(54) FORMING METHOD OF TANTALUM OXIDE FILM

(57)Abstract:

PROBLEM TO BE SOLVED: To enable a rugged part of a substrate to be coated with a tantalum oxide film of uniform thickness, even if rugged parts such as deep groove or steeply stepped part is present on the surface of the substrate.

SOLUTION: A first process, where material gas, which contains at least, pentaethoxy tantalum (Ta(OC2H5)5), is introduced into a reaction chamber where a substrate 11 is installed, a second process where tantalum pentaethoxy (Ta(OC2 H5)5) is thermally decomposed in a nonoxidizing atmosphere to form a tantalum oxide (Ta2O5) thin film 14 on the substrate 11 through a CVD method, and a third process where the substrate 11, where the tantalum oxide (Ta2O5) thin film 14 is formed, is subjected to an after process where oxygen is used are provided.



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CLAIMS

[Claim(s)]
[Claim 1] The process which introduces the material gas which contains a pentaethoxy tantalum (Ta (OC2H5)5) at least in the reaction chamber in which the substrate was installed, The process which pyrolyzes said pentaethoxy tantalum (Ta (OC2H5)5), and forms a tantalum oxide (Ta 2O5) thin film on said substrate with a CVD method under a non-oxygen ambient atmosphere, The formation approach of a tantalum oxide thin film of having the process which performs after treatment which used oxygen for the substrate with which the tantalum oxide (Ta 2O5) thin film was formed.
[Claim 2] The formation approach of the tantalum oxide thin film according to claim 1 characterized by forming a tantalum oxide (Ta 2O5) thin film on said nitride after carrying out nitriding treatment of the substrate and forming a nitride.
[Claim 3] The formation approach of the tantalum oxide thin film according to claim 1 or 2 characterized by performing the process which forms a tantalum oxide (Ta 2O5) thin film on a substrate at the temperature of 500 degrees C or less which a pentaethoxy tantalum (Ta (OC2H5)5) pyrolyzes at least.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Field of the Invention] This invention relates to the formation approach of a tantalum oxide thin film useful as capacity insulator layers, such as a DRAM capacitor, etc.
[0002]
[Description of the Prior Art] Generally membrane formation of the tantalum oxide thin film (Ta2O5 film) to a substrate top is performed using the CVD method. Drawing 6 is drawing for explaining an example of the manufacturing installation of the conventional tantalum oxide thin film. As a raw material of tantalum oxide, the pentaethoxy tantalum (Ta (OC2H5)5) which is a liquid is used, and this is held in the tank 41 in a thermostatic chamber 42. Temperature control of the tank 41 is carried out to 35 degrees C by the thermostatic chamber 42. N2 N2 supplied to the tank 41 from the charging line 48 Gas pressurizes the inside of a tank 41 and extrudes the pentaethoxy tantalum which is a liquid raw material for the feeding piping 49. A carburetor 43 is supplied from the feeding piping 49, and the pentaethoxy tantalum which is said liquid raw material is N2 in a carburetor 43. A charging line 48 to N2 Carrier gas is supplied. The material gas evaporated with the carburetor 43 is said N2. With carrier gas, it is introduced into a reaction chamber 45 through a charging line 44. Moreover, oxygen is also introduced into it and coincidence from an oxygen tank (not shown), the pyrolysis of the pentaethoxy tantalum is carried out in a reaction chamber 45, and a tantalum oxide thin film is formed on a substrate. After membrane formation, the ambient atmosphere in a reaction chamber 45 is exhausted through an exhaust pipe arrangement 47 with a pump 46.
[0003] The property in which the hole of oxygen can tend to do the tantalum oxide thin film formed by such CVD method is seen. For this reason, an impurity is captured, or the trap of the charge is carried out to that hole, and this has become one factor which generates leakage current. Therefore, in the conventional technique, oxygen was introduced as mentioned above at the time of membrane formation, and the efforts for for decreasing the hole of oxygen were paid. Furthermore, after membrane formation was performing oxygen annealing and oxygen plasma treatment in order to aim at much more reduction of the hole of oxygen.
[0004]
[Problem(s) to be Solved by the Invention] However, by the formation approach of the tantalum oxide thin film in the conventional technique, when concave heights, for example, the trench section, and the level difference section exist in a substrate, there is a trouble that it is difficult for said concave heights to cover a tantalum oxide thin film with uniform thickness. In addition, in this specification, the formation condition of a tantalum oxide thin film over concave heights will be called step coverage nature below.
[0005] The electrolysis reinforcement impressed to a capacity insulator layer as it is poor becomes uneven, and when extreme, step coverage nature will bring about increase of dielectric breakdown or leakage current, and will spoil the dependability of DRAM remarkably in the high place of electrolysis reinforcement.

[0006] now -- if membrane formation temperature becomes an elevated temperature in membrane formation of the tantalum oxide thin film using a CVD method -- a reaction -- since rate-limiting -- feeding -- a membrane formation device changes rate-limiting. In the feeding rate-limiting condition, although a reaction is mainly governed by temperature in the reaction rate-limiting condition, since the amount of supply of a raw material governs a membrane formation reaction, a membrane formation reaction is too quick, it becomes inadequate forming membranes it inside concave heights, and step coverage nature falls. Therefore, in order to make step coverage nature good, it is necessary to make membrane formation temperature low enough but so that reaction rate-limiting ****** may be carried out, and when membrane formation temperature is made low, the carbon concentration in a tantalum oxide thin film increases shortly, and there is a danger that leakage current will increase by this.
[0007] Thus, the property of the thin film obtained even if it makes high membrane formation temperature of a tantalum oxide thin film with the conventional technique and makes it low has merits and demerits, and the formation approach of a tantalum oxide thin film with good current and step coverage nature is searched for in this industry.
[0008] This invention is made in order to solve the technical problem mentioned above, and it aims at offering the formation approach of the good tantalum oxide thin film of step coverage nature.
[0009]
[Means for Solving the Problem] The process to which this invention introduces the material gas which contains a pentaethoxy tantalum (Ta (OC2H5)5) at least in the reaction chamber in which the substrate was installed, The process which pyrolyzes said pentaethoxy tantalum (Ta (OC2H5)5), and forms a tantalum oxide (Ta 2O5) thin film on said substrate with a CVD method under a non-oxygen ambient atmosphere, The formation approach of a tantalum oxide thin film of having the process which performs after treatment which used oxygen for the substrate with which the tantalum oxide (Ta 2O5) thin film was formed is offered. Moreover, after this invention carries out nitriding treatment of the substrate and forms a nitride, it offers the formation approach of the aforementioned tantalum oxide thin film characterized by forming a tantalum oxide (Ta 2O5) thin film on said nitride.
[0010] Furthermore, this invention offers the formation approach of the aforementioned tantalum oxide thin film that the process which forms a tantalum oxide (Ta 2O5) thin film on a substrate is characterized by being carried out at the temperature of 500 degrees C or less which a pentaethoxy tantalum (Ta (OC2H5)5) pyrolyzes at least.
[0011]
[Embodiment of the Invention] According to this invention, since membrane formation by the CVD method of a tantalum oxide thin film is performed under the non-oxygen ambient atmosphere, a membrane formation rate is controlled and step coverage nature improves. The problem of the hole of the oxygen by the bottom of a non-oxygen ambient atmosphere is solvable by performing after treatment which used oxygen for the substrate after the tantalum oxide thin film was formed.
[0012] If membranes are formed under a non-oxygen ambient atmosphere, the same conditions as conventional it can be used for the formation conditions of the tantalum oxide thin film in this invention. Moreover, the after treatment performed using oxygen after the tantalum oxide thin film was formed is O2. Or O3 It can carry out at the temperature of 450-800 degrees C under an ambient atmosphere. As after treatment performed using this oxygen, it is O2. Annealing treatment and UV-O3 Annealing treatment and O2 It is desirable for plasma treatment etc. to be mentioned and to perform these processings beyond need time amount.
[0013] According to this invention, by setting the membrane formation temperature in the process which forms a tantalum oxide thin film on a substrate as the temperature of 500 degrees C or less which can pyrolyze material gas at least, a membrane formation device can govern the reaction of a reaction rate limiting next door and membrane formation with temperature, and membrane formation inside [which was established in the substrate] concave heights becomes good. Furthermore, the problem of the increment in the carbon concentration in a tantalum oxide thin film is not produced, either.
[0014] In addition, a substrate front face made from the conventional, for example, polish, recon oxidizes, and it is SiO2 there. It is formed. SiO2 with a small dielectric constant Although the trouble

that the capacitor by the layer and the tantalum oxide thin film becomes series connection, and the effectual dielectric constant of the formed capacitor falls may arise In this invention, after carrying out nitriding treatment of the substrate and forming a nitride, this problem is solved by forming a tantalum oxide thin film on a nitride. In addition, although what is necessary is just to determine the thickness of a nitride suitably in consideration of the membrane formation conditions of a tantalum oxide thin film, about 20A of it is usually enough.

[0015] Here, although JP,6-61450,A which is indicating the technique similar to this invention has proposed the technique which forms a tantalum oxide thin film on a substrate with a CVD method under a non-oxygen ambient atmosphere, this conventional technique is not indicating after treatment, such as annealing under the oxygen content ambient atmosphere after membrane formation of a tantalum oxide thin film, at all. Moreover, membrane formation temperature is also an elevated temperature of 550 degrees C or more, and is not taken into consideration at all about performing membrane formation at the temperature (500 degrees C or less) by which reaction rate-limiting ****** is carried out. Moreover, it is not indicated at all about the nitriding treatment of the substrate before membrane formation of a tantalum oxide thin film.

[0016] Although the approach of this invention can be enforced using the conventional equipment previously explained by drawing 6 as it is, a tantalum oxide thin film is formed under a non-oxygen ambient atmosphere.

[0017]

[Embodiment of the Invention] Hereafter, the gestalt of operation explains this invention further. The gestalt of this operation estimated the step coverage nature of a tantalum oxide thin film. Drawing 1 is a sectional view for explaining the sample used in order to evaluate step coverage nature. On a silicon wafer 11, it is Th-SiO2 with a thickness of 200m. Boron phospho silicate glass 12 is formed through a layer 17, and the crevice is formed there. The diameter of this crevice is 0.4 micrometers and the depth is 2000nm. Moreover, the polish recon layer 13 is formed in the upper part of boron phospho silicate glass 12 by the thickness which is 30nm. The nitride 14 is formed in the upper part of the polish recon layer 13 by the thickness which is 20A. It was prepared in the upper part of a nitride 14 by the thickness whose tantalum oxide thin film 15 is 100nm, and drawing 1 has indicated, respectively by making thickness corresponding to the direction of the inside of the "a section" and a crevice for the thickness of the height direction of a substrate into the "b section." The polish recon layer 16 is further formed in the upper part of the tantalum oxide thin film 15 by the thickness which is 30nm.

[0018] Evaluation of the step coverage nature in this operation gestalt was performed by investigating the rate of the thickness of the b section to the a section of the tantalum oxide thin film 15. That is, it can be said that step coverage nature is good, so that this rate is close to 100%. Moreover, it expressed the aspect ratio described below as a ratio of the depth of a crevice to the diameter of a crevice.

[0019] Drawing 2 is drawing for explaining the relation between the aspect ratio at the time of forming a tantalum oxide thin film in a CVD method, and step coverage nature. In drawing 2 , a curve 21 shows the result at the time of forming membranes under a non-oxygen ambient atmosphere, and the curve 22 shows the result at the time of forming membranes under an oxygen content ambient atmosphere.

[0020] The membrane formation conditions at this time formed membranes under the oxygen content ambient atmosphere, membranes were formed under the non-oxygen ambient atmosphere, or, similarly except [all] set up conditions. That is, membrane formation temperature is 480 degrees C, and a membrane formation pressure is 25Pa, pentaethoxy tantalum flow rate 0.1sccm, and a carrier N2. It was referred to as oxygen flow rate 500sccm in the case of using flow rate 500sccm and oxygen.

[0021] Step coverage nature of way [when membranes are formed under an oxygen content ambient atmosphere to step coverage nature being 100% even if an aspect ratio becomes large when membranes are formed under a non-oxygen ambient atmosphere, and step coverage nature is 94% in 4 and an aspect ratio forms a tantalum oxide thin film under a non-oxygen ambient atmosphere from drawing 2] is improving.

[0022] Drawing 3 is drawing showing the relation between the membrane formation temperature at the time of forming a tantalum oxide thin film in a CVD method, and a membrane formation rate. In

drawing 3 , a curve 31 shows the result at the time of forming membranes under a non-oxygen ambient atmosphere, and the curve 32 shows the result at the time of forming membranes under an oxygen content ambient atmosphere. The membrane formation conditions at this time formed membranes under the oxygen content ambient atmosphere, membranes were formed under the non-oxygen ambient atmosphere, or, similarly except [all] set up conditions. That is, membrane formation temperature is 480 degrees C, and a membrane formation pressure is 25Pa, pentaethoxy tantalum flow rate 0.1sccm, and a carrier N2. It was referred to as oxygen flow rate 500sccm in the case of using flow rate 500sccm and oxygen.

[0023] From drawing 3 , the membrane formation rate is controlled rather than it at the time of an oxygen content ambient atmosphere, and the way of the membrane formation rate when forming membranes under a non-oxygen ambient atmosphere shows that step coverage nature becomes much more good as for this.

[0024] Drawing 4 expands the curve 31 which shows the result at the time of forming membranes under a non-oxygen ambient atmosphere in drawing 3 . Thereby, when it exceeds 500 degrees C, it turns out that curved inclination becomes loose. if, as for this, membrane formation temperature becomes an elevated temperature from 500 degrees C -- a reaction -- since rate-limiting -- feeding -- it is shown that a membrane formation device changes rate-limiting.

[0025] Drawing 5 is drawing showing the thickness distribution in 470 degrees C - 510 degrees C at the time of forming membranes under a non-oxygen ambient atmosphere, and drawing showing thickness [as opposed to a measuring point in (a)] and (b) are drawings showing a measuring point to the flow direction of gas. Compared with 470 degrees C and 500 degrees C, it turns out at 510 degrees C that thickness distribution of the flow direction of gas is changing a lot. although reaction rate-limiting ****** of this is carried out at 470 degrees C and 500 degrees C -- 510 degrees C -- a reaction -- feeding -- ruling over rate-limiting is shown.

[0026] By making membrane formation temperature into 500 degrees C or less shows that reaction rate-limiting ****** is carried out from drawing 4 and drawing 5 . This shows that step coverage nature becomes much more good by making membrane formation temperature into 500 degrees C or less. If membrane formation temperature is too low, in order for a membrane formation rate to become slow and to cause the fall of a throughput, it becomes impossible in addition, to say that it is practical. When they are taken into consideration, membrane formation temperature has desirable 420 degrees C or more. Moreover, evaluation of leakage current was performed, and the result equivalent to the former has been obtained and the problem of the increment in the carbon concentration in the tantalum oxide film is also cleared.

[0027]

[Effect of the Invention] The process to which the formation approach of the tantalum oxide thin film this invention introduces the material gas which contains a pentaethoxy tantalum (Ta (OC2H5)5) at least in the reaction chamber in which the substrate was installed, The process which pyrolyzes said pentaethoxy tantalum (Ta (OC2H5)5), and forms a tantalum oxide (Ta 2O5) thin film on said substrate with a CVD method under a non-oxygen ambient atmosphere, Since it has the process which performs after treatment [substrate / with which the tantalum oxide (Ta 2O5) thin film was formed] using oxygen, even if it is the case where concave heights, for example, the trench section, and the level difference section exist in a substrate, a tantalum oxide thin film can be covered with uniform thickness to said concave heights.

[Translation done.]

JAPANESE [JP,2000-340559,A]

CLAIMS DETAILED DESCRIPTION TECHNICAL FIELD PRIOR ART EFFECT OF THE INVENTION TECHNICAL PROBLEM MEANS DESCRIPTION OF DRAWINGS DRAWINGS

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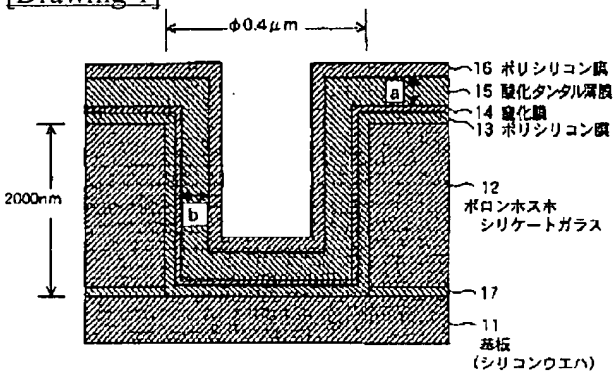
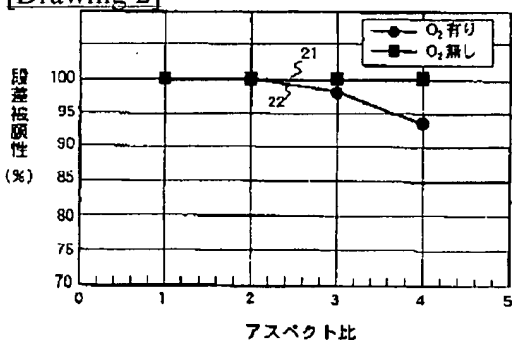
DRAWINGS

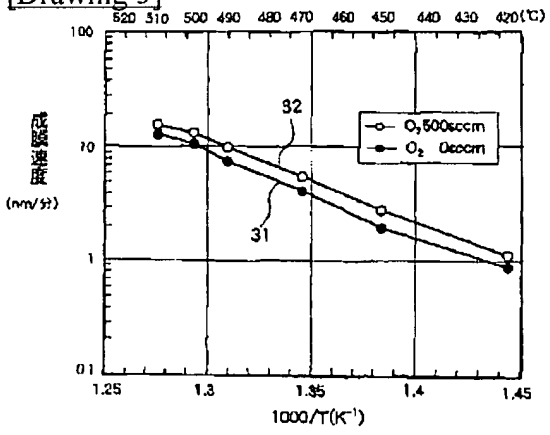
[Drawing 1]



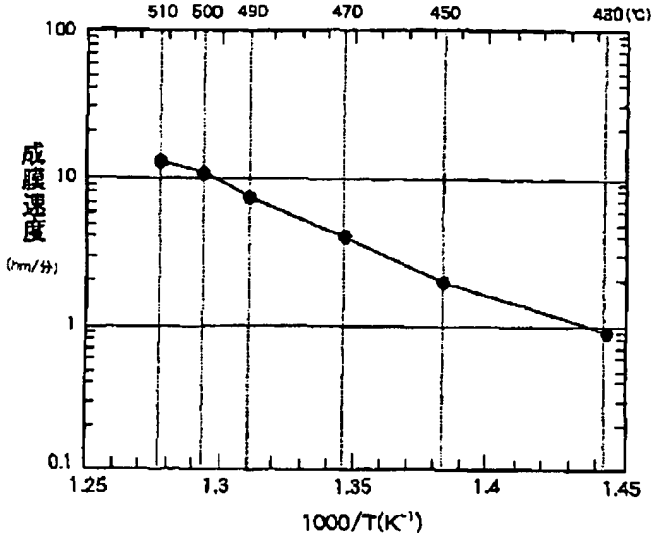
[Drawing 2]



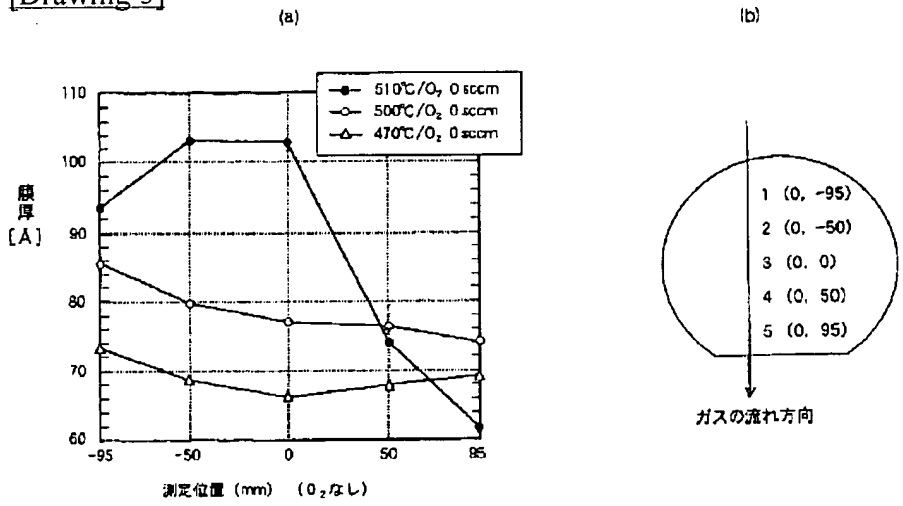
[Drawing 3]



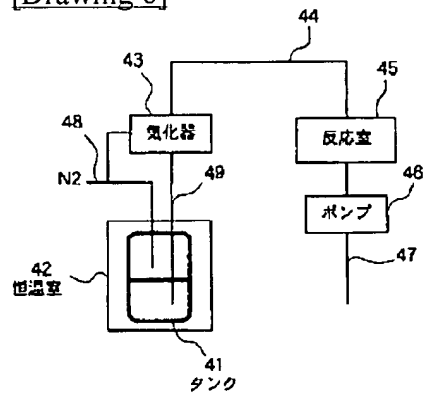
[Drawing 4]



[Drawing 5]



[Drawing 6]



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